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SYNTHESIS AND CATALYTIC PROPERTIES OF HYDROPHOBICALLY MODIFIED POLY(ALKYLMETHYL- DIALLYLAMMONIUM CHLORIDES)

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Abstract—Novel non-cross-linked and cross-linked, hydrophobically modified homo- and copolymers were synthesized by free-radical cyclo(co)polymerization of alkylmethyldiallylammonium chloride monomers in aqueous solution using ammonium persulfate as the initiator. Cross-linking was brought about by addition of a small amount of *N,N'*-methylenebisacrylamide. The cross-linked homo- and copolymers showed an increase of their reduced viscosity in aqueous solution upon the controlled introduction of cross-linking agent into their chemical structure. Viscosity measurements revealed that the conformational transition of polysoaps to compact coils in aqueous solution is strongly dependent upon the hydrophobic group content of the polysoaps. The formation of hydrophobic microdomains is akin to intramolecular micelle formation. Depending on the hydrophobic group content and the percentage of cross-linking, intermolecular aggregation was also revealed by viscosity measurements at higher concentrations of polysoap. The hydrophobic microdomains of the non-cross-linked and cross-linked polysoaps were characterized by hypsochromic shifts of the long-wavelength absorption band of Methyl Orange as a solvatochromic probe, non-covalently bound to the macromolecule. Catalysis of the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate by the non-cross-linked and cross-linked copolymers was investigated in aqueous solution at pH 11.3 and 30°C. The cross-linked polysoaps exhibited higher catalytic activities for decarboxylation than the corresponding non-cross-linked analogues. A maximum in rate constant was found at about 0.2% (w/w) of cross-linking agent in the cross-linked polysoaps. The decarboxylation rate is strongly dependent upon the hydrophobic group content in the polysoaps.

INTRODUCTION

Polyelectrolytes carrying hydrophobic side chains (polysoaps) are an interesting class of water-soluble polymers which form hydrophobic microdomains in aqueous solution [1–7]. These polysoaps retain many of the properties of the polymers from which they are derived but their physical-chemical behavior is considerably modified by the presence of the hydrophobic side chains. Hydrophobic interactions between side chains cause contractions in the molecular dimensions in aqueous solution, leading to an aggregation process which may be termed intramolecular micelle formation [7–9]. The hydrophobic microdomains, which possess properties similar to those of surfactant micelles, solubilize normally water-insoluble organic compounds such as alkanes and arenes [9, 10]. Polysoaps can also serve as efficient catalysts for many organic reactions [11–14] and the (co)polymers provide convenient systems [11, 15] for studies of the role of electrostatic and hydrophobic interactions in aqueous solutions. The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) [4, 7, 14] which is not subjected to acid and base catalysis, and particu-

larly sensitive to medium effects [16] has been widely used as a kinetic probe to study the microenvironmental effects under a variety of reaction conditions [4, 7, 11, 14, 16].

In a previous report, we described the synthesis and catalytic properties of cross-linked poly(alkylmethyldiallylammonium bromides) [7]. The present paper reports the synthesis of a series of novel non-cross-linked and cross-linked homo- and copolymers by cyclo(co)polymerization of alkylmethyldiallylammonium chlorides in which the alkyl group is methyl and *n*-dodecyl and for which cross-linking is performed with a small amount of *N,N'*-methylenebisacrylamide. Viscosity measurements provide direct evidence for the formation of both intramolecular micelles and intermolecular aggregates in aqueous solution. The conformational transitions of the polysoaps are strongly dependent upon the dodecyl group content. Pseudo-first-order rate constants for the decarboxylation of 6-NBIC catalyzed by polysoaps were determined as a function of the detailed structure of the polysoap. The decarboxylation of 6-NBIC is markedly influenced by both the dodecyl group content and the percentage of cross-linking in the polysoaps, indicating that the catalysis is sensitive to changes in the structure of the intramolecular aggregate.

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Table I. Cyclo(co)polymerization of alkylmethyldiallylammonium chlorides

Polymer	DIMDACI ^a (mol)	DMDAACI ^b (mol)	N,N'-MbisAM ^c (%, w/w)	APS ^d (mg)	Polymerization time (hr)	Yield (%)	Water solubility
PolC-1-Cl(2)	0.036	0.000	0.00	58	48	51	Soluble
CL-PolC-1-Cl(3)	0.036	0.000	0.40	58	48	76	Soluble
CL-PolC-1-Cl(4)	0.036	0.000	2.00	58	2.0	74	Gel
CL-PolC-1-Cl(5)	0.036	0.000	4.00	58	0.5	68	Gel
CopolC1-12-Cl(6)	0.036	0.004	0.00	71	48	75	Soluble
CL-CopolC1-12-Cl(7)	0.036	0.004	0.20	71	48	80	Soluble
CL-CopolC1-12-Cl(8)	0.036	0.004	0.40	71	48	78	Soluble
CL-CopolC1-12-Cl(9)	0.036	0.004	0.80	71	48	75	Soluble
CL-CopolC1-12-Cl(10)	0.038	0.002	0.40	70	48	78	Soluble
CL-CopolC1-12-Cl(11)	0.032	0.008	0.40	72	48	67	Soluble

^aDimethyldiallylammonium chloride.^bn-Dodecylmethyldiallylammonium chloride.^cN,N'-Methylenebisacrylamide(cross-linking agent).^dAmmonium persulfate.

EXPERIMENTAL PROCEDURES

Materials and monomers

The synthesis of n-dodecylmethyldiallylammonium bromide has been described previously [4, 7]. n-Dodecylmethyldiallylammonium chloride was prepared from n-dodecylmethyldiallylammonium bromide by the following procedure. An n-dodecylmethyldiallylammonium bromide [7] solution in methanol was passed through an ion-exchange column (Amberlyst A-26) in the chloride form which effectively exchanged the bromide ion for chloride ion. After evaporation of the solvent under reduced pressure, the product was dissolved in deionized water and extracted several times with diethyl ether, and finally freeze-dried for at least 2 days. Dimethyldiallylammonium chloride (Aldrich) was used as received. For the hygroscopic materials often no completely satisfactory elemental analyses could be obtained.

n-Dodecylmethyldiallylammonium chloride (DMDAACI) (I). Yield 98%; yellow oil [17]; ¹H-NMR δ 0.80 (t, 3H), 1.15–1.30 (m, 18H), 1.65–1.75 (m, 2H), 2.95 (s, 3H), 3.10–3.20 (m, 2H), 3.85–3.95 (d, 4H), 5.60–5.75 (m, 4H), 5.90–6.10 (m, 2H) ppm. Found: Cl, 11.08. C₁₉H₃₈NCl requires: Cl, 11.22.

Cyclo(co)polymerizations

A solution of the monomer in deionized water (40%, w/w) was placed in a flask equipped with a magnetic stirrer and a nitrogen inlet and outlet. After the monomer was completely dissolved, the monomer solution was polymerized in the presence of a small amount of N,N'-methylenebisacrylamide (Janssen) using commercial grade ammonium persulfate (Janssen) as the initiator at 60°C under nitrogen. In the cross-linking polymerizations the monomer ratio and content of cross-linking agent were varied. Non-cross-linked (co)polymers were also synthesized under similar polymerization conditions but in the absence of the cross-linking agent. The obtained reaction mixtures were dialysed against deionized water using dialysis tubes (Servapore dialysis tubing 29 mm) for 72 hr at room temperature. The polymer solutions were subsequently freeze-dried for at least 3 days. The obtained cross-linked and non-cross-linked (co)polymers were characterized by their i.r. and ¹H-NMR spectra. These spectra showed the complete absence of C=C double bond absorption bands and resonances, respectively, in these products. The ¹H-NMR spectra were in agreement with those reported in the literature for structurally related polymers [4, 7, 17].

All polymeric materials showed characteristic properties akin to those described previously [4, 7, 8]. Since the exact molecular weights are unknown, all polymer concentrations are expressed in unit mol/l. For the homopolymers PolC1-1-Cl and CL-PolC1-1-Cl the unit molar mass is taken as that of the dimethyldiallylammonium chloride monomer. For the copolymers the unit molar mass is defined by x (molar mass

of dimethyldiallylammonium chloride) + y (molar mass of dodecylmethyldiallylammonium chloride).

Non-cross-linked and cross-linked poly(dimethyldiallylammonium chloride) (PolC-1-Cl and CL-PolC-1-Cl). White amorphous solid; ¹H-NMR δ 1.25 (CH₂), 1.50 (CH₂), 2.15 [CH(ring, trans)], 2.60 [CH(ring, cis)], 3.00–3.25 [CH₂(N), CH₂(N), CH₂(ring, cis/trans)], 3.70 [CH₂(ring, cis/trans)] ppm.

Non-cross-linked and cross-linked poly(dimethyldiallylammonium-co-n-dodecylmethyldiallylammonium chlorides) (CopolC1-12-Cl and CL-CopolC1-12-Cl). White amorphous solid; ¹H-NMR δ 0.75 (CH₃), 1.20 (CH₂), 1.45 (CH₂), 2.20 [CH(ring, trans)], 2.60 [CH(ring, cis)], 3.00–3.25 [CH₂(N), CH₂(N), CH₂(ring, cis/trans)], 3.70 [CH₂(ring, cis/trans)] ppm.

All the CL-CopolC1-12-Cl macromolecules reported in Table 1 showed the same ¹H-NMR resonances but exhibit small differences in integrations. The molecular weights of the non-cross-linked and cross-linked copolymers are believed to be usually similar to those of the corresponding non-cross-linked and cross-linked homopolymers based on similar polymerization conditions.

i.r. and ¹H-NMR measurements

The i.r. spectra of the cross-linked and non-cross-linked (co)polymers were measured with a Perkin-Elmer 841 i.r. spectrophotometer using a KBr disc. ¹H-NMR spectra of the monomers and all water-soluble polymers were taken on a VXR 300 MHz instrument using TMS as an external reference. All NMR spectra were taken in D₂O.

Viscosity measurements

The reduced viscosities of aqueous solutions of polysoaps were measured in a capillary viscometer of the Ubbelohde type (Scott AVS 400 viscosimeter) in a constant temperature bath at 30°C and at pH ca 7.5. Plots of the reduced viscosity against polymer concentration were non-linear under these conditions. Variation of the pH between 7.0 and 12.0 had no significant effect on the measured reduced viscosities. All polymer solutions were made up in double-distilled water.

u.v.-vis spectral measurements

u.v.-vis absorption spectra of Methyl Orange (Philips PU 8740 u.v.-vis scanning spectrophotometer) were recorded in the presence of cross-linked copolymers at 30°C in aqueous solutions adjusted to pH 9.4 with a 0.02 M sodium borate buffer. The solution of Methyl Orange (2.5×10^{-5} M) was prepared with double-distilled water.

Kinetic experiments

Fresh stock solutions of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) for kinetic measurements were prepared in methanol. The reaction was initiated by mixing of 2.5 ml of the aqueous solutions of copolymers at pH 11.3 in 0.002 M NaOH with 5 μ l of the prepared stock solution of

Table 2. Compositions of non-cross-linked and cross-linked poly(dodecylmethyldiallylammonium-co-dimethyldiallylammonium) chlorides based on $^1\text{H-NMR}$

Copolymer	Feed ratio (%, mol/mol)		Found (%, mol/mol)	
	<i>n</i>	<i>m</i>	<i>x</i>	<i>y</i>
CopolC1-12-Cl(6)	90	10	89	11
CL-CopolC1-12-Cl(7)	90	10	89	11
CL-CopolC1-12-Cl(8)	90	10	90	10
CL-CopolC1-12-Cl(9)	90	10	89	11
CL-CopolC1-12-Cl(10)	95	5	95	5
CL-CopolC1-12-Cl(11)	80	20	79	21

6-NBIC (2.0×10^{-1} M) in the thermostated cell. All reactions were followed spectrophotometrically at 410 nm using a Perkin-Elmer $\lambda 2$ spectrophotometer equipped with a data station. The first-order rate constants ($\pm 1\%$) for unimolecular decarboxylation of 6-NBIC were determined from measurements for at least six half-lives at $30 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Synthesis

Cross-linked poly(alkylmethyldiallylammonium chlorides) were synthesized by free-radical cyclo(copolymerization of alkylmethyldiallylammonium chloride with a small amount of N,N' -methylenebisacrylamide using ammonium persulfate as initiator in aqueous solution (Scheme 1). The corresponding non-cross-linked polysoaps were prepared using a similar procedure but in the absence of the cross-linking agent. The results are summarized in Table 1. The water solubility of the cross-linked (co)polymers is strongly influenced by the content of the cross-linking agent. Solubility in water is restricted to (co)polymers for which the content of the cross-linking agent is in the range of *ca* 0.10–1.00% (w/w). The cross-linked (co)polymers

formed a polymer gel in aqueous solution when the cross-linking agent content exceeded 1.0% (w/w). The (co)polymers are hygroscopic materials as indicated by the presence of absorption bands of water at 3440, 2080 and 1640 cm^{-1} in their i.r. spectra. The i.r. spectra of CL-PolC-1-Cl(3) and CL-CopolC1-12-Cl(7)–CL-CopolC1-12-Cl(11) show a marked NH absorption band at 1530 cm^{-1} and the strength of the NH absorption band increases with an increase of the cross-linking agent content as compared with PolC-1-Cl(2) and CopolC1-12-Cl(6), indicative for the presence of the cross-linking agent. The macromolecules contain monomer units with 5-membered rings cross-linked with N,N' -methylenebisacrylamide on the basis of their $^1\text{H-NMR}$ spectroscopic data [4, 7, 17–19]. The cross-linked copolymer compositions, which are presumed to be random, were obtained from their $^1\text{H-NMR}$ spectra by careful integration of relevant peaks [20]. The results for all water-soluble copolymers are presented in Table 2. The compositions of these non-cross-linked and cross-linked copolymers (*x/y*) are generally in good agreement with the feed ratio of monomers in the polymerization reactions.

Viscosity behavior of the polysoaps

Measurements of reduced viscosities are particularly useful in studies of the conformational transition of polyelectrolytes to compact coils in aqueous solution [7, 21, 22]. The characteristics of the viscosity behavior of the non-cross-linked and cross-linked (co)polymers as a function of concentration in aqueous solutions is illustrated in Fig. 1. The cross-linked (co)polymers [CL-PolC-1-Cl(3) and CL-CopolC1-12-Cl(8)] exhibit larger reduced viscosities than the corresponding non-cross-linked (co)polymer analogues [PolC-1-Cl(2) and CopolC1-12-Cl(6)]. The results for PolC-1-Cl(2) and CL-PolC-1-Cl(3)

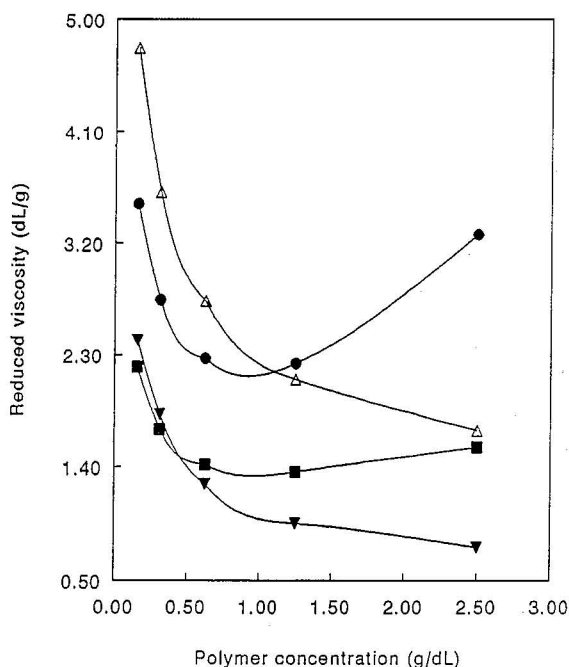
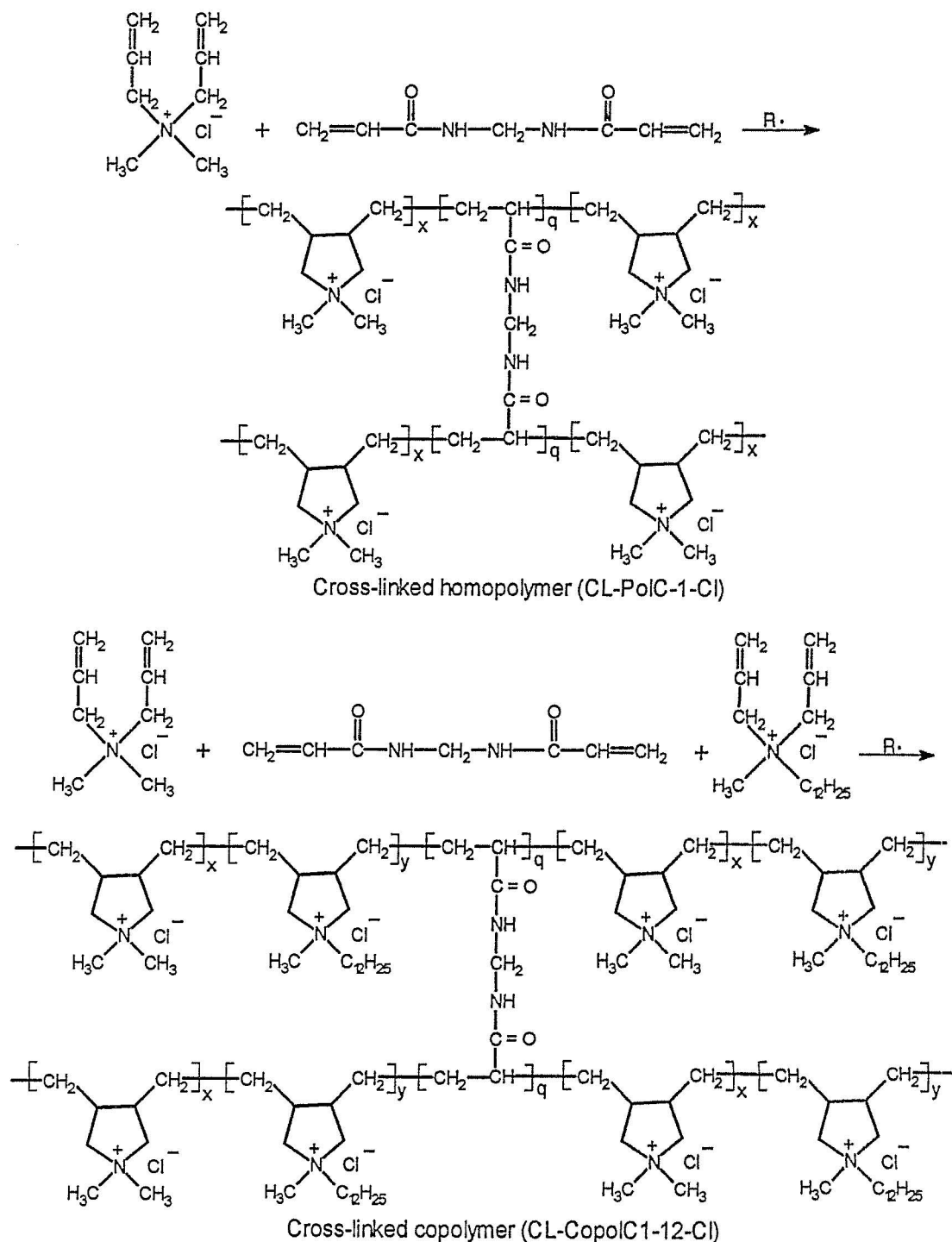


Fig. 1. Reduced viscosities (η_{sp}/c) of non-cross-linked and cross-linked (co)polymers in aqueous solution at 30°C . Δ , CL-PolC-1-Cl(3); \bullet , CL-CopolC1-12-Cl(8); \blacktriangledown , PolC-1-Cl(2); \blacksquare , CopolC1-12-Cl(6).



Scheme 1

show that the reduced viscosity in aqueous solution increases strongly with decreasing concentration, indicative for highly extended molecular dimensions typical of normal polyelectrolyte behavior. CopolC1-12-Cl(6) and CL-CopolC1-12(8) have lower reduced viscosities in aqueous solution than PolC-1-Cl(2) and CL-PolC-1(3), respectively, which indicates the presence of compact coil conformations brought about by intramolecular micelle formation [7, 22, 23]. At higher concentration, the curves of CopolC1-12-Cl(6)

and CL-CopolC1-12-Cl(8) show an increase of the reduced viscosity with increasing concentration, consistent with intermolecular aggregation via hydrophobic interactions between the dodecyl groups [22]. We note that CL-CopolC1-12-Cl(8) shows stronger intermolecular interaction than the corresponding non-cross-linked copolymer CopolC1-12-Cl(6), indicating that the intermolecular aggregation of polysoaps is markedly dependent on the detailed structure of macromolecular chains. Furthermore,

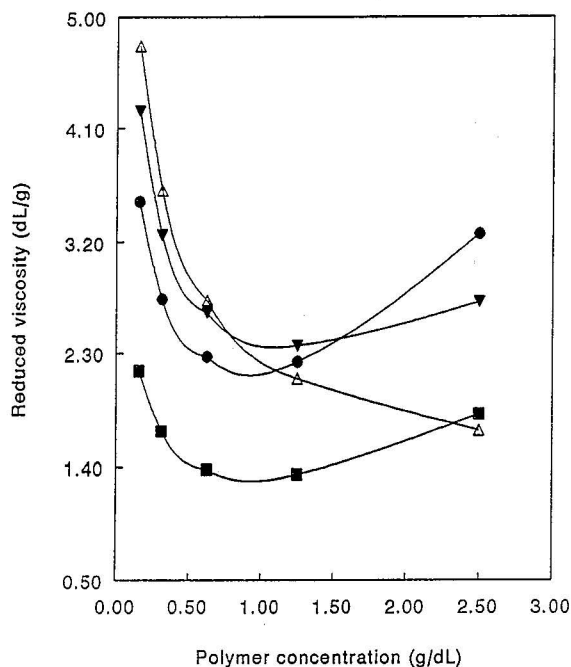


Fig. 2. Effect of the dodecyl group content on the reduced viscosity of CL-CopolC1-12-Cl containing 0.40% (w/w) of cross-linking agent in aqueous solution at 30°C. Δ , CL-PolC-1-Cl(3); \blacktriangledown , CL-CopolC1-12-Cl(10); \bullet , CL-CopolC1-12-Cl(8); \blacksquare , CL-CopolC1-12-Cl(11).

the presence of cross-linking in polysoaps leads to stronger intermolecular aggregation as compared with that for the non-cross-linked polysoap analogues. The effect of the dodecyl group content on the reduced viscosity of cross-linked (co)polymers with a constant content of cross-linking agent is shown graphically in Fig. 2. Lower reduced viscosities are

found at low polymer concentrations when the dodecyl group content in the polysoaps is increased. We contend that the conformational transition of cross-linked copolymers to compact coils is strongly dependent upon the dodecyl group content as anticipated for an aggregation process largely dictated by hydrophobic interactions. At higher concentration, CL-Co-

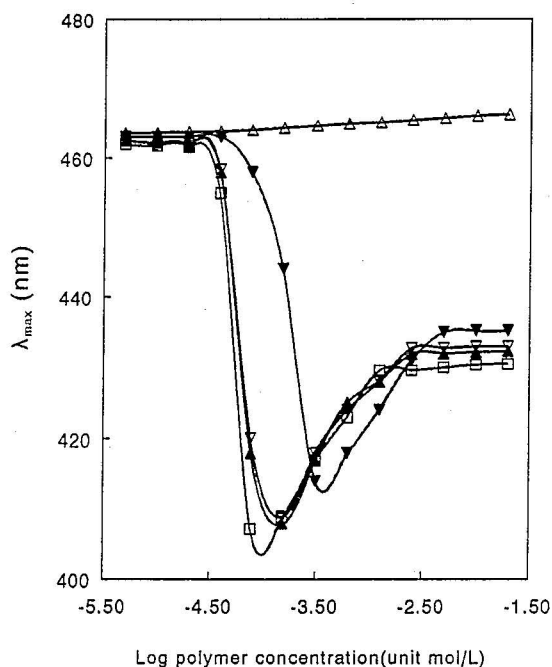


Fig. 3. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of (co)polymers at pH 9.4 and 30°C. Δ , CL-PolC-1-Cl(3); \blacktriangledown , CL-CopolC1-12-Cl(10); \blacktriangle , CL-CopolC1-12-Cl(7); ∇ , CL-CopolC1-12-Cl(8); \square , CL-CopolC1-12-Cl(11).

Table 3. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solution of non-cross-linked and cross-linked (co)polymers at pH 9.4 and 30°C

(Co)polymer	Concentration (unit mol/l)	λ_{\max}^a (nm)
PolC-1-Cl(2)	5.0×10^{-3}	466
CL-PolC-1-Cl(3)	5.0×10^{-3}	466
CopolC1-12-Cl(6)	2.5×10^{-3}	433
CL-CopolC1-12-Cl(7)	2.5×10^{-3}	431
CL-CopolC1-12-Cl(8)	2.5×10^{-3}	432
CL-CopolC1-12-Cl(9)	2.5×10^{-3}	432
CL-CopolC1-12-Cl(10)	3.0×10^{-3}	435
CL-CopolC1-12-Cl(11)	3.0×10^{-3}	430

^aMethyl Orange, 2.5×10^{-5} M; $\lambda_{\max} = 462.5$ nm in aqueous solution at pH 9.4 and 30°C.

polC1-12-Cl(8) and CL-CopolC1-12-Cl(11) exhibit a larger increase in reduced viscosity than CL-CopolC1-12-Cl(10) which suggests that intermolecular aggregation of cross-linked copolymers is also markedly affected by the dodecyl group content.

Binding of Methyl Orange to compact coils formed by the polysoaps

The hydrophobic microdomains formed by the polysoaps can be probed by using sufficiently hydrophobic dyes [4, 7, 14, 24]. We have measured the position of the long-wavelength absorption maximum of Methyl Orange in aqueous solution in the presence of cross-linked (co)polymers at pH 9.4 and 30°C (Fig. 3 and Table 3). Methyl Orange (2.5×10^{-5} M) shows an absorption maximum at 462.5 nm in aqueous 0.02 M sodium borate buffer solutions (pH 9.4) at 30°C. The hypsochromic shifts (Table 3) reveal the binding of Methyl Orange at hydrophobic binding sites in the presence of non-cross-linked and cross-linked copolymers. The data refer to relatively high polysoap concentrations where the formation of hydrophobic microdomains is not induced by the presence of the dye [8]. The non-cross-linked and cross-linked copolymers induce marked spectral shifts and these shifts increase with an increasing dodecyl group content. However, the spectral shifts are only weakly sensitive to differences in cross-linking. The data in Table 3 indicate that only the copolymers with a sufficient content of dodecyl side chains form hydrophobic microdomains in aqueous solution.

Catalysis of the decarboxylation of 6-NBIC by the polysoaps

The unimolecular decarboxylation of 6-nitrobenzoxazole-3-carboxylate anion (6-NBIC, Scheme 2) is extremely slow in an aqueous solution ($k_w = 7.35 \times 10^{-6} \text{ sec}^{-1}$, at 30°C) [25], but the reaction rate depends greatly on the reaction medium

Table 4. Kinetic parameters for the unimolecular decarboxylation of 6-NBIC in aqueous solutions in the presence of non-cross-linked and cross-linked (co)polymers at pH 11.3 and 30°C

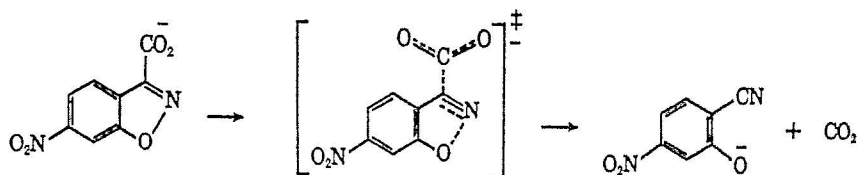
(Co)polymer	$k_m \times 10^3, \text{ sec}^{-1}$	$K, \text{ M}^{-1}$	k_m/k_w^a	γ^b
PolC-1-Cl(2)	$2.50 \cdot 10^{-2c}$		3	
CL-PolC-1-Cl(3)	$2.30 \cdot 10^{-2c}$		3	
CopolC1-12-Cl(6)	12.80	60	1741	0.995
CL-CopolC1-12-Cl(7)	14.10	63	1918	0.995
CL-CopolC1-12-Cl(8)	12.50	82	1701	0.998
CL-CopolC1-12-Cl(9)	11.20	105	1524	0.999
CL-CopolC1-12-Cl(10)	7.20	48	980	0.980
CL-CopolC1-12-Cl(11)	14.80	217	2014	0.999

^a $k_w = 7.35 \times 10^{-6} \text{ sec}^{-1}$ in aqueous solution at 30°C [26].

^bCorrelation coefficient in the Menger-Portnoy analysis [34].

^cAt 5.0×10^{-2} unit mol/l.

[26–30]. The decarboxylation of 6-NBIC has been extensively employed to investigate the microenvironment at binding sites for micellar and vesicular pseudophases [25, 27, 31] and hydrophobic microdomains in polymer solutions [4, 7, 14, 15, 32]. We have studied the unimolecular decarboxylation of 6-NBIC in the presence of non-cross-linked and cross-linked (co)polymers in aqueous solution at pH 11.3 and 39°C. The data given in Fig. 4 show that all copolymers are very efficient catalysts for decarboxylation of 6-NBIC in aqueous solution. Catalysis by the cross-linked copolymers with a high dodecyl group content exhibits a rapid enhancement of the first-order rate constants (k_d) at low concentrations of polysoap, followed by gradual leveling-off with increasing concentration. Finally, the rate constants reach plateau values. Table 4 presents the kinetic parameters for the unimolecular decarboxylation of 6-NBIC in aqueous solution in the presence of non-cross-linked and cross-linked copolymers obtained from an analysis in terms of the Menger-Portnoy model [33]. Thus, k_m is the decarboxylation rate constant for the substrate fully bound to the polysoap, and K is the equilibrium constant for the binding of 6-NBIC to the polysoap, PolC-1-Cl(2) and CL-PolC-1-Cl(3) only show a small rate enhancement, indicating that no hydrophobic microdomains are formed in this system. In these cases the kinetic data were not analyzed within the framework of the Menger-Portnoy model [15, 33] and, therefore, the rate constant for high polymer concentration is listed. The data given in Table 4 indicate that the copolymers exhibit higher catalytic efficiencies for the decarboxylation of 6-NBIC than the polysoaps with bromide counterions [7]. A likely explanation may involve smaller chloride counterion binding to the cationic groups at the periphery of the hydrophobic microdomains leading to increased initial state destabilization [16]. The results presented in Fig. 5 reveal that the percentage of cross-linking significantly



Scheme 2

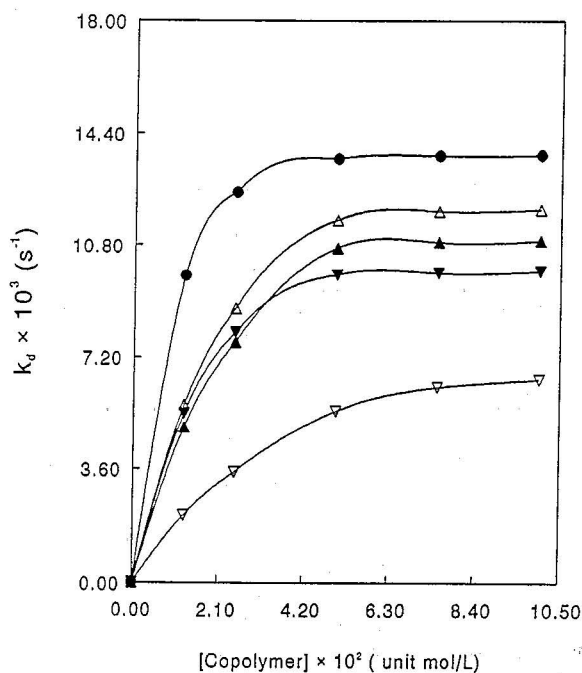


Fig. 4. Rate constants for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of non-cross-linked and cross-linked polysoaps at pH 11.3 and 30°C. ●, CL-CopolC1-12-Cl(11); △, CL-CopolC1-12-Cl(7); ▲, CopolC1-12-Cl(6); ▼, CL-CopolC1-12-Cl(9); ▽, CL-CopolC1-12-Cl(10).

affects the rate of decarboxylation of 6-NBIC in aqueous solution. A maximum of the rate constant is observed at about 0.20% (w/w) cross-linking agent. This result shows that the formation of hydrophobic microdomains of cross-linked copolymers is clearly dependent on the structure of macromolecular chain. A similar conclusion has been reached previously for

the corresponding polysoaps with bromide counterions [7]. Apparently the presence of a small amount of cross-linking in CL-CopolC1-12-Cl(7) allows more efficient intramolecular micelle formation as compared with the situation for CopolC1-12-Cl(6). The effect of the dodecyl group content of cross-linked copolymers on the decarboxylation rate of 6-NBIC in

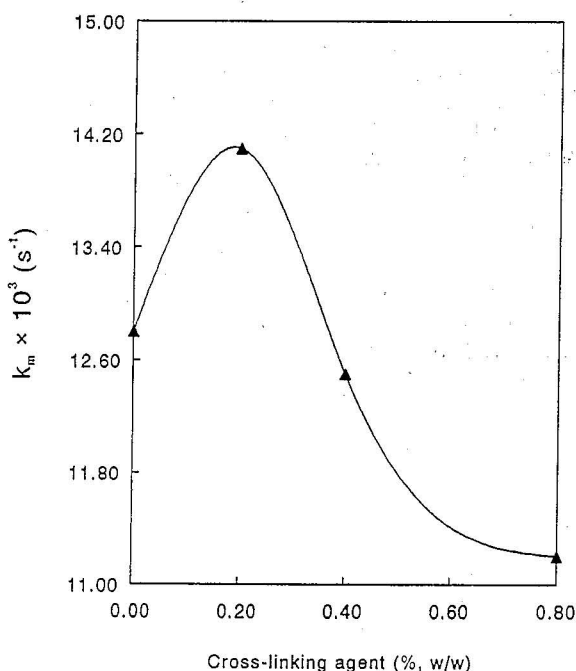


Fig. 5. Effect of cross-linking agent content on the rate constant for decarboxylation of 6-NBIC in aqueous solutions of CL-CopolC1-12-Cl(x/y , 90/10) at pH 9.4 and 30°C.

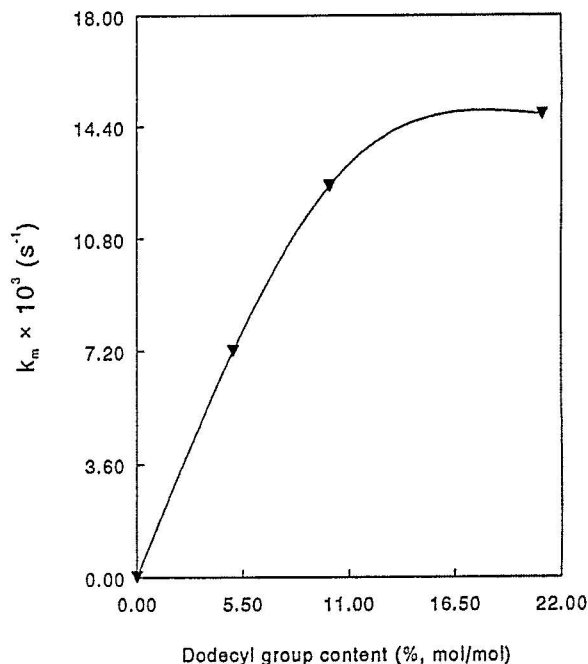


Fig. 6. Effect of the dodecyl group content on the rate constant for the decarboxylation of 6-NBIC in aqueous solutions of CL-CopolCI-12-Cl containing 0.40% (w/w) of cross-linking agent at pH 11.3 and 30°C.

aqueous solution is presented graphically in Fig. 6. The reaction rates for decarboxylation of 6-NBIC drastically increase with an increase in the dodecyl group content of cross-linked polysoaps. CL-CopolCI-12-Cl(11) shows the highest catalytic efficiency as expected on the basis of the results of viscosity measurements.

CONCLUSION

Previous studies [7] have shown that the unimolecular decarboxylation of 6-nitrobenzoxazole-3-carboxylate is efficiently catalyzed by the cross-linked poly(alkylmethyldiallylammonium bromides) and responds to changes in the detailed structure and aggregation properties of the macromolecules. The present study shows that the cross-linked poly(alkylmethyldiallylammonium chlorides) are more efficient catalysts for the decarboxylation of 6-NBIC than the corresponding cross-linked poly(alkylmethyldiallylammonium bromides). The intramolecular micelle formation and intermolecular aggregation clearly depend on the detailed structure and aggregation properties of the macromolecules. The presence of a small amount of cross-linking allows more efficient intramolecular micelle formation as compared with non-cross-linked copolymer analogues. Measurements of the reduced viscosities indicate that the conformational transition of cross-linked copolymers to compact coils is strongly influenced by the dodecyl group content. The cross-linked copolymers show stronger intermolecular hydrophobic aggregation than the corresponding non-cross-linked copolymers.

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